**Pore-scale simulation of coupled multiple physicochemical thermal processes in micro reactor for hydrogen production using lattice Boltzmann method**

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**A B S T R A C T**

A general numerical scheme based on the lattice Boltzmann method (LBM) is established to investigate coupled multiple physicochemical thermal processes at the pore-scale, in which several sets of distribution functions are introduced to simulate fluid flow, mass transport, heat transfer and chemical reaction. Interactions among these processes are also considered. The scheme is then employed to study the reactive transport in a posted micro reactor. Specially, ammonia (NH₃) decomposition, which can generate hydrogen (H₂) for fuel of proton exchange membrane fuel cells (PEMFCs), is considered where the endothermic decomposition reaction takes place at the surface of posts covered with catalysts. Simulation results show that pore-scale phenomena are well captured and the coupled processes are clearly predicted. Effects of several operating and geometrical conditions including NH₃ flow rate, operating temperature, post size, post insert position, post orientation, post arrangement and post orientation on the coupled physicochemical thermal processes are assessed in terms of NH₃ conversion, temperature uniformity, H₂ flow rate and subsequent current density generated in PEMFC.

1. Introduction

Micro reactors are well-defined miniaturized devices with characteristic dimensions from sub-millimeter to sub-micrometer [1,2], and they have been commercially used for a wide range of applications such as chemical synthesis and chemical decomposition. Carrying out chemical reactions in micro-reactors offers several inherent advantages, including large surface area to volume ratio, high heat and mass transfer rate, minimal substance consumption and precisely controlled reactive conditions, thus generating increased yield and selectivity of the desired products [3,4]. In micro-reactors, the surface area to volume ratio scales inversely as the characteristic length of the micro-reactor, and is several orders of magnitude higher than that of traditional chemical reactors [5]. This striking feature is especially desirable for applications in which expensive porous catalytic inserts (such as platinum) are required [6]. In micro-reactors, several physicochemical and thermal processes, including fluid flow, species diffusion, heat transfer and chemical reaction, simultaneously take place. The flow characteristics obviously play important roles on mass and heat transfer; local mass and heat transfer significantly
affects the chemical reaction; in turn, chemical reaction has
great impacts on local species concentration and temperature
distributions, as it directly determines the amount of mass
generation (or consumption) and heat released (or absorbed). In
general, these processes are closely related to and coupled with
each other, and can be called coupled multiple physicochemi-
cal and thermal processes.

Numerical simulations have been demonstrated as an
especially effective and powerful tool for understanding the
coupled multiple physicochemical and thermal processes in
micro-reactors. Based on whether the actual morphology of
porous catalytic inserts is explicitly considered or not, simula-
tions concerning reactive transport processes in micro
reactors can be divided into two major categories: macro
simulations solving the conservation equations volume-
averaged over each elementary volume assuming a homoge-
neous porous structures with isotropic or anisotropic trans-
port properties [7–10]; and pore-scale simulations
incorporating realistic or approximately realistic microstruc-
tures of porous structures [11–21]. Compared to macro
simulations based on the continuity assumptions which
usually employ macro geometrical parameters as well as
empirical relations between macro geometrical parameters and
macro transport properties (such as relations between
permeability and porosity), pore-scale simulations can
explicitly resolve the realistic microstructures and describe
the transport without making any assumption about the
effects of the microstructures on the macro transport prop-
ties. They can be used to improve the fundamental under-
standing of the transport processes in porous domain. The
growing evidence of the importance of pore-scale simulations
is reflected in the increasing interest in modeling fluid flow
and transport phenomena in porous structures in micro
reactors [11–22].

Among the numerical methods adopted for implementa-
tion of pore-scale simulations, the lattice Boltzmann method
(LBM) is a promising and effective alternative. The LBM
considers flows to be a collective behavior of pseudo-particles
residing on a mesoscopic level, and solves Boltzmann equa-
tion using a small number of velocities adapted to a regular
grid in space. Due to its underlying kinetic nature, the LBM
has been found to be particularly useful in fluid flow applications
involving interfacial dynamics and complex boundaries, e.g.
multiphase or multicomponent flows in porous media [23].
Recently, there have been some studies using the LBM to
investigate hydrodynamics and transport phenomena in
reactors or micro-reactors. Zeiser et al. [14] performed simu-
lations of isothermal fluid flow in a 3D tube filled with spheri-
cated catalyst. Mass transport and chemical reaction,
however, was simulated in a simple 2D system consisted of
a channel with a square block, rather than in the 3D tube filled
with catalyst. Lately, Freund et al. [15] applied LBM to simulate
isothermal fluid flow and mass transport in randomly packed
fixed-bed reactors, where a first-order chemical reaction
occurring at the surface of the particles was considered.
Sullivan et al. [16] studied fluid flow, mass transport and reaction
in a packed-bed micro-reactor, where a wide range of Pe and
Re as well as various ratios between intra- and inter-particle
diffusivity were considered. However, the simulations were
isothermal and therefore thermal effects were ignored in their
studies. Kao et al. [17] investigated fluid flow and heat transfer
in fixed-bed micro-reactors at the pore-scale using LBM.
However, in their study mass transport and chemical reaction
was not considered, and chemical reaction efficiency was
roughly evaluated using a simple model based on the
temperature field obtained in the LBM simulations. Manjhi
et al. [18] employed LBM to investigate fluid flow and transient
concentration distributions in a tube filled with adsorbents
and their simulation results displayed the breakthrough
curves of concentration as well as uniform concentration
distribution across the cross-section of the tube. Lately, the
same group extended their LB model by considering the micro
mass transport inside the porous adsorbents [19], and further
by taking into account the heat transfer [20]. Yang et al. [24]
studied biochemical reaction in a micro channel reactor,
representing the practical process of hydrogen production by
photosynthetic bacteria (PSB) in bio-film bioreactors. In
their study, they assumed that released heat from the biochemical
reaction was negligible. Based on the above literature review,
it can be found that most previous studies considered fluid
flow, heat transfer, mass transport and chemical reaction
separately, and research work based on LBM involving all the
coupled multiple physicochemical and thermal processes in
reactive micro-flows is limited. Indeed, the highly coupled
characteristics of these processes pose great challenges to
developing corresponding numerical models.

In the present study, the high-temperature catalytic gas-
phase reaction of NH₃ decomposition using Ni–Pt/Al₂O₃ as
catalyst is considered, which can produce hydrogen (H₂) as
fuel for proton exchange membrane fuel cells (PEMFCs) [25].
The PEMFC has been considered as an alternative power
source for various applications and has caught much atten-
dition during the past decades [26]. One of the main obstacles for
wide commercialization of the PEMFC is the hydrogen supply.
Several processes have been proposed for producing hydrogen
[27]. Among them, producing hydrogen from the single-step
decomposition of NH₃ proves to be attractive as NH₃ has
high hydrogen content and the process does not generate COx
that is not environment friendly [25,28]. Besides, the tech-
niques for product, transport and storage of NH₃ are quite
mature at present. In addition, using small-scale micro-rec-
tors to decompose NH₃ is especially suitable for supplying H₂
to PEMFCs, as PEMFCs are usually used as power sources for
portable mobile electrical devices and vehicles in which power
source with small size is desirable.

The objectives of the present study are to: (1) establish a
coupled LB algorithm and framework that is capable of
simulating coupled multiple physicochemical and thermal
processes at pore-scale; (2) investigate the pore-scale multiple
physicochemical and thermal phenomena and the coupled
mechanism in micro reactors; (3) delineate the effects of
operating and geometrical conditions on reactor performance
and improve the conversion efficiency of the chemical reac-
tion. The rest of the present paper is arranged as follows. In
Section 2 governing equations at the pore-scale, LB model,
chemical reaction model, conjugate heat transfer, computa-
tional domain, and boundary conditions are introduced. In
Section 3 the LB modeling scheme developed is used to
simulate transport phenomena in a posted micro reactor.
Finally, some conclusions are drawn in Section 4.
2. Model description

2.1. Governing equations at pore-scale

The following assumptions are made for simulating the coupled multiple physicochemical and thermal processes taking place in a micro reactor. (1) The fluid flow is considered incompressible and laminar because the Re in the micro reactor is small (0-1.25 in the present study, calculated using inlet velocity and gap between posts). (2) Heat and mass transfer has limited effects on fluid flow. Therefore, the coupling between the flow and heat/mass transfer is one-way, and the simulation of flow field is decoupled from the simulation of temperature and concentration field. The flow field numerically predicted is superimposed on the modeling of heat and mass transfer. Based on the above assumption, the governing equations at the pore-scale for the mass conservation, fluid flow, heat and mass transfer inside the micro-reactor can be written as

\[ \nabla (u) = 0 \]  
(1)

\[ \rho \nabla (uu) = -\nabla p + \nabla \cdot (\nabla u) \]  
(2)

\[ \nabla (uC) = \nabla \cdot [(D_{eff} \nabla C) + S_t] \]  
(3)

\[ \nabla (uT) = \nabla \left( \frac{\lambda}{\rho C_p} \nabla T \right) + S_t \]  
(4)

where \( u, p, T, C_i \) are the local velocity, pressure, temperature and concentration of the \( i \)th species in the gas mixture, respectively. The source terms of Eqs. (3) and (4) \( S_t \) and \( S_r \) will be discussed later.

Based on the assumption of ideal gas mixture, the mass-weighted density \( \rho \) are calculated by

\[ \rho = \sum_i C_i M_i \]  
(5)

where \( M_i \) is the molecular weight of \( i \)th species. Besides, specific heat \( c_p \) and dynamic viscosity \( \mu \) of the gas mixture are calculated using mass weighted mixing law

\[ c_p = \sum_i m_i c_{pi}, \quad \mu = \sum_i m_i \mu_i \]  
(6)

where \( m_i, c_{pi} \) and \( \mu_i \) are mass fraction, specific heat of the \( i \)th species and dynamic viscosity of the \( i \)th species, respectively. The conductivity \( \lambda \) in the void space can be calculated using mass weighted mixing law as that in Eq. (6), while that in the solid space is set as the conductivity of solid post. The transport properties of individual species are computed using kinetic theory and the specific heat of gases is calculated using piecewise-polyhedral relations.

2.2. Numerical method

LBM is used to solve the above governing equations. The general LB pore-scale model for simulating reactive transport in porous media with multiple aqueous components and minerals developed by Kang et al. [29,30] are adopted in the present study. This model takes into account advection, diffusion, and homogeneous reactions among multiple aqueous species, heterogeneous reactions between the aqueous solution and minerals, as well as the resulting geometrical changes in pore space. However, no thermal effect was considered in their model. In the present study, we enhance this model by accounting for heat transfer process.

2.2.1. LBM for fluid flow

The LB fluid flow model employed is based on the simple and popular Bhatnagar–Gross–Krook (BGK) method [31]. DnQb lattice is adopted where \( n \) denotes the dimension and \( b \) represents number of discrete velocities [32,33]. The evolution of LB equation is described by

\[ f_i(x + c_i \Delta t, t + \Delta t) - f_i(x, t) = -\frac{1}{\tau_s} \left( f_i(x, t) - f_i^{eq}(x, t) \right) \]  
(7)

where \( f_i(x, t) \) is the particle distribution function with velocity \( c_i \) at the lattice site \( x \) and time \( t \), \( f_i^{eq} \) is the ith equilibrium distribution function, \( \Delta t \) is the time increment, and \( \tau_s \) is the collision time. \( c_i \) is the discrete velocities. For D2Q9 model used in this study, \( c_i \) is given by

\[ c_i = \begin{cases} 0 & i = 0, (i-1)\pi \sin \left( \frac{(i-1)\pi}{2} \right) \quad i = 1, 2, 3, 4 \\ \sqrt{2} \cos \left( \frac{(i-5)\pi}{2} \right) \sin \left( \frac{(i-5)\pi}{4} \right) & i = 5, 6, 7, 8 \end{cases} \]  
(8)

The equilibrium distribution function is given by

\[ f_i^{eq} = \omega_i \rho \left[ 1 + \frac{3}{2c_i^2} (c_i \cdot u)^2 + \frac{9}{2c_i^4} (c_i \cdot u)^4 \right] \]  
(9)

where the weights \( \omega_i = 4/9, i = 0; \omega_i = 1/9, i = 1, 2, 3, 4; \omega_i = 1/36, i = 5, 6, 7, 8 \). \( c_i \) is the speed of sound \( c_i = c/\sqrt{3} \) where \( c \) equals \( \Delta s/\Delta t \). Fluid density \( \rho \) and velocity \( u \) can be obtained from the first and second moments of the particle distribution functions

\[ \rho = \sum_i f_i \]  
(10)

\[ \rho u = \sum_i f_i c_i \]  
(11)

The kinematics viscosity in lattice unit is related to the collision time by

\[ v = c_s^2 \left( \tau_s - 0.5 \right) \Delta t \]  
(12)

2.2.2. LBM for mass transport

The following evolution of LB equation is used to describe species transport [34]

\[ g_i(x + c_1 x + c_i \Delta t, t + \Delta t) - g_i(x, t) = -\frac{1}{\tau_s} \left( g_i(x, t) - g_i^{eq}(x, t) \right) \]  
(13)

where \( g_i \) is the concentration distribution function of \( k \)th component in the direction \( i \). The equilibrium concentration distribution function \( g_i^{eq} \) is commonly chosen

\[ g_i^{eq} = C_i [J_i + K_i c_i \cdot u] \]  
(14)

where \( K_i \) is constant and equals 1/2 for two-dimensional case, and \( C_i \) is the concentration.
For mass transport simulation, the D2Q9 square lattice for 2D simulation can be reduced to D2QS square lattice by ignoring velocities at the diagonals, namely the four velocities with subscript i greater than 4 in Eq. (8). This reduction of discrete velocities doesn’t create loss of accuracy [16,30].

\[ J_i \text{ in Eq. (14) is given by [16]} \]

\[ J_i = \begin{cases} J_{0i} \quad & i = 0 \\ \left(1 - J_{0i}\right)/4, & i = 1, 2, 3, 4 \end{cases} \tag{15} \]

where the rest fraction \( J_{0i} \) can be selected from 0 to 1 and is set as 0.2 in the present study. Species concentration \( C \) is obtained by

\[ C_i = \sum g_{ik} \tag{16} \]

The diffusivity in lattice unit is related to the collision time by

\[ D_k = \frac{C_\text{eq}(1 - J_{0k})(\tau_{2k} - 0.5) \langle \Delta x^2 \rangle}{\Delta t} \tag{17} \]

where \( C_\text{eq} \) is a lattice dependent coefficient and equals 1/2 for 2D simulation [16].

Eqs. (13) and (14) can be recovered to advection-diffusion Eq. (3) for concentration using Chapman–Enskog expansion.

### 2.2.3. LB model for heat transfer

Drawing analogy with the transport for a species, the LB equation for the heat transfer is

\[ h_i(\mathbf{x} + \mathbf{c}_i \Delta t, t + \Delta t) - h_i(\mathbf{x}, t) = -\frac{1}{\tau_h} (h_i(\mathbf{x}, t) - h_i^{eq}(\mathbf{x}, t)) + J_i \Delta t S_T \tag{18} \]

where \( h_i \) is the temperature distribution function. The equilibrium distribution function \( h_i^{eq} \) with D2QS square lattice is similar to Eq. (14)

\[ h_i^{eq} = T [ \mu_{i\tau} + K_{\tau\tau} \mathbf{c} \cdot \mathbf{u} ] \tag{19} \]

where the rest fraction \( K_{\tau} \) also can be selected from 0 to 1 depending on the thermal diffusivity \( \alpha \), and \( J_i, T \) is determined similar to that in Eq. (15). Note that in solid phase velocity is zero and so is the second term at the right hand of Eq. (19). Temperature \( T \) is obtained by

\[ T = \sum h_i \tag{20} \]

The thermal diffusivity \( \alpha \) in lattice unit is related to the collision time by

\[ \alpha = \frac{1}{2}(1 - K_{\tau\tau}) (\tau_h - 0.5) \langle \Delta x^2 \rangle / \Delta t \tag{21} \]

The governing equation for temperature Eq. (4) can be obtained from Eqs. (18) and (19) using Chapman–Enskog expansion method.

### 2.3. Chemical reaction model

Chemical reactions can be roughly divided into two categories, namely exothermic reactions generating heat and endothermic reaction absorbing heat. Numerous reactions, including may notable and industrially related reactions, have been successfully operated in micro reactors [4]. In the present study, the chemical reaction considered is \( \text{NH}_3 \) catalytic decomposition using Ni–Pt/Al_2O_3 as the catalyst, which is expressed as

\[ \text{NH}_3 \rightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \tag{22} \]

Using Ni–Pt/Al_2O_3 as the catalyst, Chellappa et al. [25] performed experimental studies and suggested that the reaction rate depends solely on the \( \text{NH}_3 \) concentration when the reactor is operated around the atmospheric pressure. Inhibition effects of \( \text{H}_2 \) which will reduce the reaction rate can be neglected. Thus, 1st order kinetics for ammonia decomposition is reasonable to describe the reaction kinetics of \( \text{NH}_3 \) decomposition, which is expressed as

\[ S_{\text{NH}_3} = A_1 \exp(-E/RT)(C_{\text{NH}_3}/R \cdot T) \tag{23} \]

where \( A_1 \) is a parameter depending on the catalyst density and is \( 1 \times 10^{14} \) in the present study. \( R \) is the gas constant. \( E \) is the activation energy and is set as 196,681 J/mol [25].

Correspondingly, the hydrogen generation rate due to the reaction is given by

\[ S_{\text{H}_2} = \frac{3}{2} A_1 R T \exp(-E/RT)(C_{\text{NH}_3}/R \cdot T) \tag{24} \]

It is worth mentioning that although only \( \text{NH}_3 \) decomposition is simulated in the present study, the numerical model established is very general and can be used for other kinds of chemical reactions, as long as the corresponding chemical reaction mechanisms are known.

### 2.4. Conjugate heat transfer at the fluid-solid interface

In the present study effects of temperature on reaction rate, transport properties such as species diffusivity, specific heat, and thermal conductivity are considered. Note that effects of temperature on dynamic viscosity are ignored based on Assumption 1 in Section 2.1. Considering the importance of temperature, an accuracy prediction of temperature distribution in the computational domain is required.

Conjugate heat transfer occurs when a fluid flows along a conducting solid wall. Heat transfer condition at the solid–fluid interface can hardly be prescribed as it depends on the flow dynamics and wall properties. The simple boundary conditions, such as constant wall temperature or constant heat flux, are not suitable because heat conduction in the solids also is important to the overall heat transfer. Rather, the reasonable boundary condition at the fluid-solid interface is the fluid-solid conjugate heat transfer condition, which satisfies both temperature and heat flux continuity. Such conjugate boundary condition can be easily implemented in LBM by solving a single thermal LB equation (Eq. (18)) with different distribution functions and collision times (thermal diffusivity) for solid and fluid phase [35].

At the fluid-solid interface, heat is absorbed due to endothermic reaction of \( \text{NH}_3 \) decomposition. Thus, source term in Eq. (4) at the fluid-solid interface is

\[ S_T = k_{\text{NH}_3} \Delta H / (\rho C_P) \tag{25} \]

where \( \Delta H \) equals –46.7 kJ/mol. At other place without reaction, source term in Eq. (4) is zero.
2.5. Computational domain and boundary conditions

It is found that the flow and heat transfer performances of randomly packed grains may not be optimal, and the pressure drops in such packed grains are usually much higher than those in regularly packed ones [12,13]. Thus, in the present study, posted micro reactors with regular post arrangement are studied. Nevertheless, the present model can be directly employed to simulate the coupled physicochemical and thermal processes in complex porous structures in randomly packed reactors, due to the simple and powerful boundary treatment schemes of LBM.

In posted micro reactors, posts with pillar-like structures are arranged in the channel with several rows, and are covered with catalyst at the surface [1,2]. The computational domain in the present study is a 2D channel filled with posted catalytic inserts, as shown in Fig. 1. The width and length of the channel is 14 mm and 4.8 mm respectively. The length of the region with catalytic inserts is about 9.4 mm. The length before the catalyst region \((L_1)\) is 2 mm and that after the catalyst region \((L_2)\) is about 2.6 mm. The catalytic inserts are micro arrays of square posts (black squares in Fig. 1). Each catalytic post is a \(a\times a\) mm square with a mm gap between the adjacent posts in both \(x\) and \(y\) directions. The surfaces of the square posts are catalytic where heterogeneous NH3 decomposition reaction occurs, while the walls of the channel are set to be non-catalytic. Micro reactor with similar structures and dimensions is adopted to study propane combustion in Ref. [21] and to study ammonia decomposition in Ref. [22].

At the channel inlet, velocity with Poiseuille distribution profile is specified, with an averaged velocity varied in the range of 0.0–0.125 m s\(^{-1}\). Correspondingly, the Reynolds number \(Re\) (calculated using the size of the post as characteristic length) is in the range of 0–1.25. Besides, uniform temperature \(T_{inlet}\) is adopted. Uniform NH3 concentration fraction with value of 1 \((C_{NH3}/C_{Total,in})\), where \(C_{Total,in} = p_{in}/RT\) and \(p_{in}\) is the inlet pressure) is adopted. The \(H_2\) concentration fraction is zero \((C_{H2}/C_{Total,in})\). In LBM, the inlet velocity condition is obtained by using the scheme proposed in Ref. [36].

At the channel outlet, fully developed boundary condition is employed, which is achieved by setting the unknown distribution functions as that of the closest neighboring node within the computation domain.

At the top and bottom walls, zero-species flux and no-slip boundary condition are used for species transport and fluid flow, respectively, while temperature is set the same as temperature at the inlet.

At the fluid-solid (post) interface within the computational domain, no-slip boundary condition is applied for fluid flow. Mass transport is only considered in the void space between the posts while mass transport inside the posts is not considered as the inner pores of the posts are extremely small [22]. Heat transfer in both void and solid space is simulated using the method introduced in Section 2.5.

We roughly estimate the Knudsen number, which is defined as the ratio of mean free path (chosen as the mean free path of NH3 atmospheric pressure and temperature, about 50 nm) to the characteristic length (chosen as the gap between posts, 0.2 mm), and its value is about 0.00025. This value is smaller than the critical value 0.001, below which fluid flow is considered to be in the continuum regime. Thus, phenomena in the slip-flow regime such as slip flow, temperature jump and concentration jump does not occur in the present study.

2.6. Numerical implementation procedure

The computational domain is meshed by \(701 \times 241\) lattices which are sufficient after grid-dependency tests. The main steps for performing the simulation are as follows: (1) translating variables in physical units to lattice units using the schemes in Ref. [37]; (2) simulating the flow field using fluid flow LB model; (3) simulating the species transport and heat transfer in the superimposed flow field predicted in Step (2); (4) calculating information of concern such as temperature uniformity and chemical reaction efficiency based on the simulated results.

The simulation convergence is considered to be obtained if the relative error between successive 200 iterated steps is less than 1 \(\times 10^{-6}\). The code developed for fluid flow and mass transport has been validated in several reactive transport problems in our previous work including diffusion in a rectangular domain with chemical reaction at a boundary [30], diffusion in a rectangular domain with bulk reaction [37,38], multiple component advection-diffusion-reaction in an open channel [30]. Drawing analogy between heat transfer and mass transport, code further developed for heat transfer is dependable and its validation is not presented here for simplicity.

3. Results and discussion

Now attention is turned to investigate the coupled multiple physicochemical and thermal processes in the posted micro reactor at pore-scale and elucidate the effects of operating and geometrical conditions on reactor performance. Table 1 gives the parameter values used in the simulations, where bold numbers are values for the base case and parameters are kept at these bolded values unless otherwise stated. In this section, first the pore-scale distributions of flow field, temperature and species concentration for the base case are presented. Then effects of several operating and geometrical parameters on the hydrodynamics and transport processes are assessed in terms of breakthrough curves, temperature non-uniformity, NH3 conversion and generated H2 flow rate. Corresponding contours of temperature, \(H_2\) concentration and NH3 concentration are presented and discussed. Breakthrough curves can be used as a diagnosis of the fluid flow and mass transport.
Table 1 – Parameters in the simulation.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel length</td>
<td>L</td>
<td>14 mm</td>
</tr>
<tr>
<td>Channel width</td>
<td>W</td>
<td>4.8 mm</td>
</tr>
<tr>
<td>Catalytic region length</td>
<td>Lc</td>
<td>9.4 mm</td>
</tr>
<tr>
<td>Catalytic post width</td>
<td>a</td>
<td>120, 160, 200, 240, (or gap between posts)</td>
</tr>
<tr>
<td>Inlet NH₃ flow rate</td>
<td>Qᵢn</td>
<td>5, 28, 56, 113, 170 ml min⁻¹</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>p</td>
<td>1 atm</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>T</td>
<td>600, 700, 800, 870, 900 K</td>
</tr>
</tbody>
</table>

processes. Temperature non-uniformity δ, calculated in the catalytic region using

\[ \delta = \frac{\sum T_{\text{ave}} - T(i,j)}{N \sum T_{\text{ave}}} \]  

(26)

where \( T_{\text{ave}} \) and \( N \) is the averaged temperature and number of lattices in the catalytic region, respectively, helps to understand the heat transfer process in the reactor. High \( \delta \) denotes poor uniformity of distribution. NH₃ conversion \( \eta \), defined as

\[ \eta = \frac{C_{\text{NH₃,in}} - C_{\text{NH₃,out}}}{C_{\text{NH₃,in}}} \]  

(27)

is a global indicator for the coupled multiple processes and is useful for comprehensively assessing the reactor performance. Generated \( H₂ \) flow rate \( Qₜ \), expressed as

\[ Qₜ = C_{\text{H₂, out}} u_{\text{out}} A \]  

(28)

where \( u_{\text{out}} \) is the averaged fluid flow rate at the micro reactor outlet and \( A \) is the cross-section area of the micro reactor (we assume the reactor depth in the direction perpendicular to paper is equal to its width), is employed to evaluate the capacity of the micro reactor for the power source of a PEMFC. Considering a group of micro reactors with number \( n \) (simply chosen as 10) is used to supply \( H₂ \) to a PEMFC with fuel cell area \( A_{fc} \) (set as \( 5 \times 5 \) cm² in the present study, typical dimensions of a micro PEMFC), the current density \( I \) generated with the \( H₂ \) flow rate is

\[ I = n Qₜ \frac{2 \mathcal{F}}{A_{fc}} \]  

(29)

where \( \mathcal{F} \) is the Faraday constant (96,485 C mol⁻¹) and 2 denotes that each \( H₂ \) molecule can provide two electrons.

3.1. Fluid flow, species transport and heat transfer for the base case

Fig. 2 shows the velocity vectors (Fig. 2(a)), normalized temperature \((T/T_{\text{inlet}})\), normalized \( \text{NH₃} \) concentration \((C_{\text{NH₃}}/C_{\text{total,in}})\), and normalized \( \text{H₂} \) concentration \((C_{\text{H₂}}/C_{\text{total,in}})\) (Fig. 2(b)) distributions for the base case. As observed in the entire channel as well as in the local zoomed region, fluid flow with Poiseuille distribution profile enters the micro reactor, develops into several small quasi-Poiseuille flows between the posts, and finally leaves the micro reactor with the fully developed parabolic profile as expected. The pore-scale flow in the entire reactor is fully resolved using the LB model. Another observation of fluid flow is that no Carmen vortex is generated after the posts due to the low \( Re \) and thus the fluid flow is steady-state, validating Assumption 1 in Section 2.1. Due to different local chemical reaction rates, temperature is not uniformly distributed and undergoes a 0.25 (271.5 K) change across the whole micro reactor despite the small scale simulated, proving the necessity of non-isothermal simulations. The temperature in the center of the reactor is much lower than that around the peripheral boundaries (Fig. 2(b)). This is attributed to the endothermic reaction as well as the slow heat transfer between fluid and solid posts within the catalytic region. At the solid–fluid interface, contours of temperature fluctuate due to different thermal conductivity of fluid and solid. Lower temperature within the catalytic region is not desirable for \( \text{NH₃} \) decomposition and local heat transfer there must be enhanced. It is worth mentioning that 2D simulation somewhat exaggerate the non-uniformity of temperature, because heat conduction between posts and the other two walls of the reactor channel (namely channel walls in the third dimension which is not involved due to 2D simulation) is not considered. For the concentration distribution, the effects of velocities with parabolic profiles on the concentration distributions in the micro reactor are evident. Concentration of \( \text{NH₃} \) is higher at the central region of the channel as fast flow there leads to shorter residence time and thus local lower decomposition rate. Correspondingly, concentration of \( \text{H₂} \) is lower at the central region than that around the peripheral region.

3.2. Effects of operating conditions

3.2.1. Effects of \( \text{NH₃} \) inlet flow rate

In this section, averaged inlet velocity is changed from 0.0 to 0.125 m s⁻¹ to investigate effects of \( \text{NH₃} \) flow rate on reactive transport in the micro reactor. The corresponding flow rate of \( \text{NH₃} \) at the inlet is 0–170 ml min⁻¹ (suppose the depth of the channel is the same as its width). Fig. 3(a) describes the breakthrough curves for different \( \text{NH₃} \) flow rate, where \( y \) axis is \( \text{NH₃} \) conversion \( \eta \). It can be seen that \( \eta \) gradually increases to a constant value for all the cases, implying that reactive transport within the micro reactor continuously propagates towards the channel outlet and finally reaches steady-state operation. The higher the \( \text{NH₃} \) flow rate, the earlier the breakthrough occurs, due to the fast fluid flow. The conversion decreases as \( \text{NH₃} \) flow rate increases, as residence time of \( \text{NH₃} \) inside the reactor is shorter for higher flow rate, which qualitatively agrees with the experimental results in [25]. A quantitative agreement will require identical arrangements of catalysts within the micro-reactor in the present study and in [25].

Before presenting the temperature uniformity curves, the temperature distributions for different \( \text{NH₃} \) flow rate are displayed (that for the base case has been shown in Fig. 2(b)) for better understanding the reaction taking place in the micro reactor. Three distinct observations can be made from the set of images. First, temperature within the catalytic region is lower compared with peripheral regions, due to endothermic reaction and slow local heat transfer between fluid and solid as mentioned above. Second, region with minimum temperature moves towards the downstream as the flow rate
increases, implying that the reaction region is pushed downstream by the fast fluid flow. Third, the area of the reaction region increases as the flow rate increases. The above observations indicate that under low flow rate NH3 conversion can be completed in a small area near the entrance of the catalytic region due to sufficient residence time of NH3 in that area, while under high flow rate a longer channel is required for the thorough decomposition of NH3. Also, as the flow rate increases, the minimum temperature decreases and the temperature distribution is less uniform, as shown in Fig. 3(b) and more clearly in Fig. 3(c). This is because although fast fluid flow associated enhances the convective heat transfer within the catalytic region, the temperature distribution is dominated by heat absorption. The above observations of temperature distributions demonstrate the significance of heat transfer on reactive transport and prove the necessity of non-isothermal simulations.

Fig. 3(d) shows the effects of NH3 flow rate on H2 flow rate and current density calculated using Eq. (29). It can be seen that higher flow rate, although resulting in lower NH3 conversion as shown in Fig. 3(a), leads to a higher H2 flow rate which thus subsequently outputs higher current density in the PEMFC. This is because under higher flow rate, more NH3 is supplied to the reactor, and more H2 is generated during the same amount of time, even though not all NH3 can be fully decomposed.

In summary, higher NH3 flow rate results in lower NH3 conversion and thus more catalysts for complete decomposition, but shorter breakthrough time, higher H2 flow rate and higher current density outputted to PEMFC. Therefore, there is a tradeoff between NH3 conversion and H2 flow rate. We can say, although not rigorously, that for cases where a stable and relatively low power source is required, such as mobile phone and laptop, low NH3 flow rate operation may be desirable as it can save the catalyst; while for the case requiring a relatively high power and a quick response to power change, such as vehicle where acceleration and deceleration frequently occur, high NH3 flow rate operation may be preferred.

3.2.2. Effects of operating temperature

As mentioned in Section 2.5, temperature affects the transport properties as well as the reaction rate. In this section, operating temperature, namely the inlet temperature and the wall temperature, is changed from 600 to 900 K to elucidate its effects on performance of the micro reactor.

Fig. 4(a)–(c) show the breakthrough curves, temperature non-uniformity, H2 flow rate and current density under different operating temperatures, respectively. Fig. 4(a) shows that NH3 conversion rises sharply as temperature increases, because increasing temperature significantly increases the reaction rate, which agrees with experimental results in Ref. [25]. NH3 decomposition even does not start when
operating temperature is decreased to 700 K. The difference in breakthrough time, however, is not evident, although the operating temperature undergoes a wide change of 300 K. This is because convection dominates the mass transport and the enhancement of diffusion due to increased temperature has slight effects. Fig. 4(b) shows that temperature uniformity increases as operating temperature drops, due to the small amount of heat absorbed as low operating temperature slows.
down reaction. Fig. 4(c) shows that both H2 flow rate and current density rise as operating temperature increases, as expected. Overall, operating micro reactor under higher temperature is more desirable.

3.3. Effects of geometrical conditions

Besides operating conditions, the geometrical conditions of the porous catalytic inserts also have significant effects on reactor performance. Studying the effects of geometrical conditions will greatly help to the design of micro reactor. For heterogeneous catalytic reaction taking place at the post surface, surface area of catalysts is another important characteristic parameter besides porosity and tortuosity. In this section, effects of post size, post insert position, post arrangement and post orientation on the micro reactor performance are investigated.

3.3.1. Effects of post size

Post size (or catalyst grain size) is an important factor that influences coupled processes in the micro reactor. In this section, the side length of the square posts (also the gap between neighboring posts) is changed in the range of 120–480 μm, as listed in Table 1, while the tortuosity and entire porosity of the catalytic region remains unchanged. Under these conditions, for posts with side length $a_1$ and $a_2$, respectively, surface area of the former is $a_2/a_1$ times that of the latter, indicating reducing the post size will increase the reactive surface area.

Fig. 5(a) shows the distributions of normalized H2 concentration in the micro reactor for various post sizes. It can be seen that as post size reduces, more H2 is generated due to increased reactive surface area. Besides, the concentration front is pushed forward and becomes sharper as post size decreases, indicating that the breakthrough at the center of the channel is accelerated, due to faster fluid flow at the center. Fig. 5(b) shows that the NH3 conversion increases and the breakthrough time decreases as the post size decreases, as expected. Fig. 5(c) shows that more uniform temperature distribution is obtained as post size increases, due to less heat consumed as decomposition reaction is reduced. Fig. 5(d) shows the small pore size generates high H2 flow rate and current density, which is not surprising. In fact, decreasing the post size meets one of the prominent characteristic of micro reactor, namely improving the surface area to volume ratio. Overall, reducing the post size increases the reactive surface area and thus improves the performance of micro reactor.

3.3.2. Effects of post insert position in partially filled channel

It has been reported that fixing porous medium at different positions of a channel results in different flow and heat transfer characteristics [39–41]. In this section, the reactor channel is partially filled with porous inserts to investigate effects of positions of porous inserts on reactor performance. Post number in the y direction is gradually decreased from 10 (base case as shown in Fig. 2) to 4 with an interval of 2, and two cases of insert positions are considered. For case 1, two sets of porous catalytic inserts each with post number $n$ in the y direction are adhered to the top and bottom wall, respectively, as shown in Fig. 6(a). For case 2, one set of porous catalytic inserts with post number 2$n$ in the y direction are arranged at the centerline of the channel, as shown in Fig. 6(b).

Fig. 6(a) and (b) shows distributions of temperature, normalized NH3 concentration and H2 concentration in the reactor for the two cases with total post number of 6 in the y direction. As seen in the set of images in Fig. 6, both temperature and species concentrations show very different distributions, indicating the significant effects of catalytic insert
Fig. 5 – Effects of post size, (a) Contours of H$_2$ normalized concentration, (b) Breakthrough curves, (c) Temperature non-uniformity, (d) H$_2$ flow rate and current density.
Fig. 6 – Effects of post insert position in partially filled channel with total post number in the y direction of 6. (a) Distributions of temperature, NH$_3$ normalized concentration and H$_2$ normalized concentration for posts near the wall and (b) Distributions of temperature, NH$_3$ normalized concentration and H$_2$ normalized concentration for posts at the center; (c) Breakthrough curves, (d) Temperature non-uniformity, (e) H$_2$ flow rate and current density.
positions on the reactive transport. Obviously, partially filling the channel greatly changes the flow field. Fluid flow in the region free of posts in case 1 is faster than its counterpart in case 2, leading to sharper contours of concentration in that region for case 1. Correspondingly, fluid flow in the porous region is slower and thus residence time of NH₃ in porous region is longer for case 1, leading to larger NH₃ conversion and thus generating more H₂. Fig. 6(c) displays the breakthrough curves for both cases with different post numbers, showing that for the same number of posts Case 1 is always superior to Case 2. This can be explained by longer residence time and higher temperature in porous region for Case 1. Interestingly, for Case 1 a considerable decrease of post number only slightly reduces the NH₃ conversion. This can be explained as follows. Reducing the number of posts in Case 1 results in two factors with opposite effects on the NH₃ decomposition efficiency. The negative factor is the decrease of reactive surface area which reduces the NH₃ conversion. The positive one is the increase of residence time in the catalytic region. As the positive factor dominates the negative one, reducing post number in Case 1 has slight effects on the reaction efficiency. On the other hand, for Case 2, NH₃ conversion is more sensitive to post number and it greatly drops as post number reduces. This is because the negative factor that decreases reactive surface area dominates the positive one that increases residence time.

Although more heat is consumed in Case 1 as chemical reaction is more thorough, the temperature distribution is more uniform compared to Case 2, as shown in Fig. 6(a) with (b). This is because heat from the top and bottom walls can be more easily transferred into the porous region for Case 1. Fig. 6(c) further demonstrates the more uniformly distributed temperature for Case 1.

Finally, Fig. 6(e) displays the H₂ flow rate and current density for the two cases with different post numbers. As expected, H₂ flow rate and current density of Case 1 is greater than that of Case 2. The relatively stable operation with the decrease of the post number for Case 1 can also be observed.

Actually, there are some experiments on methanol conversion in packed-bed and wall-coated micro reactors [42–44]. These experiments found that under the same catalyst loading and methanol flow rate, the wall-coated reactor can yield higher conversion than (for reactor channel with relatively large diameter, 4 mm in Ref. [42,44]) or comparable conversion to (for reactor channel with relatively small diameter, 1 mm in Ref. [42,44]) the packed-bed reactor. Karim et al. [42] and Lee et al. [43] explained that temperature distribution within the reactor greatly affects the methanol conversion, and for reactor channel with relatively large diameter the temperature near the reactor surface is much higher than that inside the reactor. In the present study, the micro reactor with arrangement of Case 1 can be roughly considered as a wall-coated reactor. Our simulation results agree well with [42,44] that fixing catalysts near the reactor wall are beneficial for obtaining high reactor performance. In addition, our simulation results of detailed distributions of temperature and concentration reveal another reason for the superiority of wall-coated reactor, namely the slower fluid flow near the reactor peripheral wall which leads to longer residence time for chemical reaction.

Besides, it is well known that granular packing of spheres in tubes generates the so-called ‘wall effects’ phenomenon, i.e., the porosity near the tube wall is higher than that near the center of the tube and local fluid flow near the tube is relatively fast [9]. According to the conclusion of the present study that the absence of posts near the wall can greatly degrade the reactor performance, such wall effects negatively affect the reactor performance. Thus, more careful treatment should be devoted to the arrangements of catalyst grains near the wall.

3.3.3. Effects of post arrangements

In-line arrangement of posts is considered for all the cases discussed so far. In this section, different post arrangements are considered. First, posts are arranged in a staggered pattern as shown in Fig. 7(b). Second, posts are arranged in a random manner as shown in Fig. 7(c). The post size, the total porosity as well as the area of reactive surface for the staggered and random arrangements are kept exactly the same as the base case.

Fig. 7(a)–(c) shows velocity in x direction (u) for in-line, staggered, and random arrangement of posts, respectively. Comparing the velocity contours in Fig. 7(a)–(c) with each other, we can find that the staggered arrangement leads to enhanced flow behind the posts, and the random arrangement causes more heterogeneous complex flow in the catalytic region. Such different flow fields lead to different NH₃ conversion as shown in Fig. 7(d). The staggered arrangement results in the highest decomposition efficiency 0.677, followed by the random arrangement 0.666, and finally the in-line arrangement 0.656. Note that when comparing the performance of in-line arrangement and staggered arrangement, it is important to keep the reactive surface exactly the same. In Ref. [21], Retagte and Kaisare also studied the effects of in-line and staggered arrangements of posts in a micro reactor on propane conversion. In their staggered arrangement, however, the number of posts in each staggered column was one less than that in its adjacent regular column; and thus the performance of staggered arrangement was inferior to the in-line arrangement due to reduced reactive surface area. The missing posts in Ref. [21] were located near the channel wall. Based on the discussion in Section 3.3.2, neglecting the posts near the channel wall will greatly reduce the conversion efficiency due to long retentive time there. We also performed the simulations where the two half posts in staggered columns (shown in the circles in Fig. 7(b)) were removed, which is the same structure of staggered arrangement as that in Ref. [21]. The simulation results show that the corresponding NH₃ conversion is only 0.594, significantly lower than that of the in-line arrangement, confirming the importance of the posts near the wall.

For the random arrangement, its NH₃ conversion is higher than that of the in-line arrangement, which is not surprising because heterogeneous fluid flow in this arrangement leads to static flow in a wide area of the catalytic region where residence time is sufficiently long. However, it cannot be simply concluded that random arrangement always leads to better reaction efficiency than the regular arrangement, because the reaction efficiency depends heavily on the specific structures of the porous catalytic inserts and cannot be generally concluded, as confirmed by our additional simulations.
3.3.4. Effects of post orientation
Finally, the effects of post orientation are explored by rotating the posts in the base case 45° clockwise (herein diagonal arrangement). Such diagonal arrangement is widely adopted in the experiments [1, 2]. Note that such rotation will lead to fewer computational grids on the surface of each post, because the distance between two neighboring grids on the side of each post after rotation is $\sqrt{2}$ times of that before rotation. Thus, source terms of concentration and temperature is multiplied by $\sqrt{2}$ during the simulations for such diagonal arrangement, thus guaranteeing both the porosity and reactive surface area unchanged compared to the base case. The simulated NH$_3$ conversion is 0.671, slightly higher than the base case, indicating that such orientation is beneficial for NH$_3$ conversion. It is worth mentioning that the diagonal arrangement and the staggered arrangement result in higher pressure drop compared to the base case, and there is usually a tradeoff between conversion and pressure drop. Based on the simulation results in this section as well as that in the previous sections, the following design principles can be proposed for optimizing the structures of post micro reactor to improve NH$_3$ conversion and reduce catalyst amount. The posts should be smaller, fixed near the reactor walls with staggered diagonal arrangement.

4. Conclusion
In the present study, a general numerical scheme based on the LBM is established to simulate coupled multiple physicochemical thermal processes widely existing in engineering and science. In this scheme, fluid flow, heat transfer and mass transport combined with chemical reaction, as well as the interactions among these processes are taken into account. The numerical scheme is applied to investigate the pore-scale reactive transport and heat transfer processes in a posted micro reactor. The chemical reaction considered in the micro reactor is NH$_3$ decomposition reaction for generating H$_2$. The simulation results show that the numerical scheme can efficiently capture the pore-scale phenomena and predict the coupled physicochemical thermal processes. Effects of several operating and geometrical conditions on reaction efficiency are investigated. The main conclusions are listed below.

1. Increasing NH$_3$ flow rate decreases the NH$_3$ conversion and reduces the uniformity of temperature distributions; but can generate high H$_2$ flow rate which thus can output more current density in a PEMFC. Operating the micro reactor under high or low NH$_3$ conversion depends on where the micro reactor is used.

2. Operating the micro reactor under high temperature is desirable as it leads to high NH$_3$ conversion and high H$_2$ flow rate.

3. Post size greatly affects the reaction efficiency in the micro reactor and decreasing the post size helps to improve the reactor performance as it can increases the surface area to volume ratio.

4. Fixing the porous catalytic inserts near the wall or at the center of the micro reactor has a significant impact on the
reaction efficiency. For the same post number, fixing porous catalytic inserts near the wall leads to higher NH3 conversion compared with that at the center. More attention should be devoted to the porous structures near the wall, as absence of posts near the wall leads to great reduction of reaction.

(5) Post arrangement in the micro reactor plays important roles on the reaction. NH3 conversion of the staggered arrangement is higher than that of the in-line arrangement, while that of the random arrangement depends on the specific structures of the porous catalytic inserts and cannot be generally concluded. Keeping the same reactive surface area is significantly important when comparing the performance of in-line and staggered arrangements. Neglecting the posts near the channel wall in the staggered columns will greatly reduce the NH3 conversion.

In summary, our current simulation results show that for better conversion, the posters should be smaller and arranged near the reactor walls with staggered diagonal formation. It is concluded from our study that numeral modeling can help gain a better understanding of the pore-scale complex coupled physicochemical thermal processes in micro reactors, and hence can help design micro reactor for better performance and durability.

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